

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 732 416 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
25.02.2004 Bulletin 2004/09

(51) Int Cl.7: C22C 5/04

(21) Application number: 96301812.2

(22) Date of filing: 15.03.1996

(54) Refractory superalloys

Refraktäre Superlegierungen

Superalliages refractaires

(84) Designated Contracting States:
BE CH DE FR GB IT LI NL

- Murakami, Hideyuki
Tsukuba-shi, Ibaraki (JP)
- Harada, Hiroshi
Tsukuba-shi, Ibaraki (JP)

(30) Priority: 15.03.1995 JP 5568895

(74) Representative: Woodman, Derek
Frank B. Dehn & Co.,
European Patent Attorneys,
179 Queen Victoria Street
London EC4V 4EL (GB)

(43) Date of publication of application:
18.09.1996 Bulletin 1996/38

(56) References cited:

(73) Proprietor: NATIONAL RESEARCH INSTITUTE
FOR METALS
Tsukuba-shi, Ibaraki (JP)

EP-A- 0 412 171	EP-A- 0 425 679
GB-A- 1 051 224	GB-A- 2 243 372
US-A- 3 429 698	US-A- 3 904 404
US-A- 3 918 965	

• T.B. MASSALSKI: "BINARY ALLOY PHASE
DIAGRAMS" 1987, ASM, OHIO, US
XP002002590 *PAGES 1292, 1341, 1424, 1433,
1435, 1437, 1439, 1441, 1691, 1977, 1979, 1982
and 1986*

(72) Inventors:

- Koizumi, Yutaka
Tsukuba-shi, Ibaraki (JP)
- Yamabe, Yoko
Tsukuba-shi, Ibaraki (JP)
- Ro, Yoshikazu
Tsukuba-shi, Ibaraki (JP)
- Maruko, Tomohiro
Tsukuba-shi, Ibaraki (JP)
- Nakazawa, Shizuo
Tsukuba-shi, Ibaraki (JP)

EP 0 732 416 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention relates to refractory superalloys. More particularly, the present invention relates to use of superalloys as heat-resisting materials appropriate to a turbine blade or vane provided with a power-generation gas turbine, a jet engine or a rocket engine.

[0002] Ni-based superalloys have conventionally been applied to heat-resisting members provided with a high-temperature appliance such as a turbine blade or vane. These Ni-based superalloys have a melting point of around 1300°C, and therefore, the upper limit of a temperature range in which these superalloys have sufficient practical strength is at best about 1100°C. In order to improve the generated output and thermal efficiency of the high-temperature appliance, it is obligatory to increase the gas combustion temperature. The upper limit of a practicable temperature range should also be increased to a value higher than the 1100°C of the Ni-based superalloys. A material having improved heat-resisting performance is required in order to upgrade such an upper limit.

[0003] Conventional alloys containing tungsten, niobium, molybdenum or tantalum have been studied in order to realise such a property, but these alloys have a decisive defect in that they are apt to disappear due to rapid oxidation in such an oxidative atmosphere as air and a combustion gas, though they show sufficient high-temperature strength in a non-oxidative atmosphere, such as in a vacuum or an inert gas. It is therefore not possible for these alloys to be successfully applied to structural members of high-temperature appliances.

[0004] The present invention provides the use of a superalloy consisting of a primary constituent selected from the group consisting of iridium and rhodium, and one or more additive elements selected from the group consisting of titanium and aluminum when said primary constituent is iridium, and selected from the group consisting of niobium and tantalum when said primary constituent is rhodium, and wherein the total amount of said one or more additive elements in either case is within a range of from 2 to 22 atom %, said refractory superalloy having a microstructure containing an FCC-type crystalline structure phase and an Li_2 -type crystalline structure phase, as heat-resisting materials.

[0005] The present invention also provides a novel superalloy consisting of iridium and aluminum, wherein an FCC-type crystalline structure phase and an Li_2 -type crystalline structure phase are precipitated, and wherein the total amount of said aluminum is within a range of from 2 to 22 atom %.

[0006] Some embodiments of the invention will now be described by way of examples and with reference to the accompanying drawings, in which:-

30 Fig. 1 depicts strain-stress curves of refractory superalloys of the present invention and a conventional superalloy.

[0007] Refractory superalloys which meet the required performance, i.e., high-temperature strength and oxidation resistance are realised by adding one or more additive element selected from the group consisting of titanium and aluminum when the primary constituent is iridium, and selected from the group consisting of niobium and tantalum when the primary constituent is rhodium. Two crystalline phases, one of which is an FCC-type structure and the other an Li_2 -type structure, are formed in these superalloys.

[0008] As these two crystalline phases are coherent with each other, the coherent interfaces between the phases prevent movement of the dislocations and thus the high-temperature strength of the refractory superalloys reaches a maximum value. The refractory superalloys are, on the other hand, liable to become a single crystalline phase of the FCC-type structure in cases where the total amount of the additive element(s) is less than 2 atom %. Likewise, the refractory superalloys turn into single-phase alloys consisting of the Li_2 -type structure above 22 atom %. The total amount of additive element is therefore in a range of from 2 to 22 atom %.

[0009] It is possible but not according to the present invention which is defined by the claims that while the feature of the refractory superalloys in the crystalline structure is preserved, several properties including high-temperature strength and oxidation resistance are enhanced by adding some other elements.

[0010] For example, one or more reinforcing elements such as molybdenum, tungsten or rhenium may be added. This element is usually added to such heat-resisting materials as heat-resisting steels and Ni-based heat-resisting superalloys, and is known for a remarkable improvement in the high-temperature strength of such materials. Partial replacement of iridium or rhodium with ruthenium, palladium, platinum or osmium may be effective at enhancing the high-temperature strength.

[0011] For the purpose of further improving both the oxidation and high-temperature corrosion resistances, one or more elements such as chromium or rhenium which, in general, have a good effect on the oxidation resistance of heat-resisting alloys may be added.

[0012] In order to make these refractory superalloys, methods such as directional solidification, a single-crystal solidification or powder metallurgy are adopted as are used to enhance the strength of Ni-based heat-resisting superalloys. Such methods control the crystalline structure of the refractory superalloys.

[0013] In addition, methods such as solution treatment, an aging treatment, or a thermo-mechanical treatment as is common in the manufacture of two-phase alloys may be employed in order to develop properties of the refractory

superalloys by controlling their microstructure. Superalloys which contain iridium as the primary constituent, aluminum as the additive element and have FCC-type and Li_2 -type crystalline structure phases constitute a new alloy system which has never been known before.

5 EXAMPLES

[0014] Each of titanium and aluminum in the amount of 15 atom % was added to iridium and each of niobium and tantalum in the amount of 15 atom % was added to rhodium. Alloys were prepared by an arc melting. The resultant four kinds of alloy were compared with MarM247, a conventional Ni-based superalloy, for high-temperature strength.

10 These five alloys were also compared for oxidation resistance with MarM247, pure iridium, a niobium alloy, a tantalum alloy, a molybdenum alloy and a tungsten alloy.

[0015] For high-temperature strength, compression tests were carried out in air both at 1200°C and at 1800°C.

[0016] As is clear from Fig. 1, each refractory superalloy which contains iridium or rhodium as a primary element demonstrates a very high stress against deformation induced from outside. This fact makes sure that the refractory 15 superalloys are increased in strength compared with the conventional Ni-based superalloy.

[0017] Regarding oxidation resistance, oxidation losses at 1500°C for an hour were measured. Table 1 shows the amount of oxidation loss and 0.2% yield stress at 1200°C for each alloy. It is confirmed in Table 1 that the refractory superalloys of the present invention are excellent in oxidation resistance, while their strength is equal or superior to the conventional metals or alloys such as MarM247, pure iridium, a niobium alloy, a tantalum alloy, a molybdenum 20 alloy, and a tungsten alloy.

Table 1

Alloys	1200°C 0.2% yield stress (MPa)	1800°C 0.2% yield stress (MPa)	1500°C 1h oxidation loss (%)
<New alloys>			
Ir-15%Al	350	-	0.25
Ir-15%Ti	310	221.7	0.62
Rh-15%Nb	240	-	0.04
Rh-15%Ta	260	-	0.06
<Conventional alloys>			
MarM247 (Ni-based superalloy)	55	melted	melted
Pure Ir	170*	20.3	0.54
FS-85 (Nb alloy)	190*	39	100
Mo-50Re (Mo alloy)	290*	-	100
T-222 (Ta alloy)	370*	94	100
W-25Re (W alloy)	385*	133	100

* From literature

45 **Claims**

1. Use of a superalloy consisting of a primary constituent selected from the group consisting of iridium and rhodium, and one or more additive elements selected from the group consisting of titanium and aluminum when said primary constituent is iridium, and selected from the group consisting of niobium and tantalum when said primary constituent is rhodium, and wherein the total amount of said one or more additive elements in either case is within a range of from 2 to 22 atom %, said refractory superalloy having a microstructure containing an FCC-type crystalline structure phase and an Li_2 -type crystalline structure phase, as a heat-resistant material.
2. A refractory superalloy consisting of iridium and aluminum, and wherein the total amount of said aluminum is within a range of from 2 to 22 atom %, said refractory superalloy having a microstructure containing an FCC-type crystalline structure phase and an Li_2 -type crystalline structure phase.

Patentansprüche

1. Verwendung einer Superlegierung, die aus einem Hauptbestandteil, ausgewählt aus der Gruppe, bestehend aus Iridium und Rhodium, und einem oder mehreren zusätzlichen Elementen, ausgewählt aus der Gruppe, bestehend aus Titan und Aluminium, wenn der genannte Hauptbestandteil Iridium ist, und ausgewählt aus der Gruppe, bestehend aus Niob und Tantal, wenn der genannte Hauptbestandteil Rhodium ist, besteht und bei der die Gesamtmenge der genannten ein oder mehreren zusätzlichen Elementen in jedem Fall innerhalb eines Bereichs von 2 bis 22 Atom-% liegt, wobei die genannte hitzebeständige Superlegierung eine Mikrostruktur besitzt, die eine kristalline Strukturphase vom FCC-Typ und eine kristalline Strukturphase vom Ll_2 -Typ enthält, als hitzebeständiges Material.
- 10 2. Hitzebeständige Superlegierung, die aus Iridium und Aluminium besteht und bei der die Gesamtmenge des genannten Aluminiums innerhalb eines Bereichs von 2 bis 22 Atom-% liegt, wobei die genannte hitzebeständige Superlegierung eine Mikrostruktur besitzt, die eine kristalline Strukturphase vom FCC-Typ und eine kristalline Strukturphase vom Ll_2 -Typ enthält.

15

Revendications

1. Utilisation d'un superalliage constitué d'un constituant primaire choisi parmi le groupe constitué de l'iridium et du rhodium, et un ou plusieurs éléments additionnels choisis parmi le groupe constitué du titane et de l'aluminium quand ledit constituant primaire est l'iridium et choisis parmi le groupe constitué du niobium et du tantalum quand ledit constituant primaire est le rhodium et dans lequel la quantité totale desdits un ou plusieurs éléments est située dans chaque cas dans une plage allant de 2 à 22 % atomiques, ledit superalliage réfractaire ayant une microstructure contenant une phase de structure cristalline de type FCC et une phase de structure cristalline de type Ll_2 , à titre de matière résistant à la chaleur.
- 20 2. Superalliage réfractaire constitué d'iridium et d'aluminium, et dans lequel la quantité d'alliage totale dudit aluminium est située dans une plage allant de 2 à 22 % atomiques, ledit superalliage réfractaire ayant une microstructure contenant une phase de structure cristalline de type FCC et une phase de structure cristalline de type Ll_2 .
- 25

30

35

40

45

50

55

Fig. 1

